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(54) Abstract Title
Adhesive containing calcium sulphate

(57) A composition for admixing with water to form an adhesive, comprises:

(A) anhydrous and/or partially hydrated calcium sulphate;

(B) a hardening-rate modifier to regulate the rate of setting of the composition when admixed with water;

(C) a water-retention aid;

(D) a rheology modifier; and

(E) a water-soluble or redispersible polymer resin.

A cellulose ether, starch ether or gum may constitute both (C) and (D) and (D) may also be a bentonite clay, wollastonite or attapulgite.

The compositions may be used for adhering ceramic tiles to a substrate.

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ADHESIVE

This invention relates to adhesive compositions, particularly but not exclusively for adhering ceramic tiles or the like to a substrate.

It is often desired to adhere ceramic tiles directly to gypsum-based substrates, such as floors and walls. The use of adhesives based on portland cement for this purpose has not hitherto been successful due to reaction of tricalcium aluminate in the portland cement with water soluble salts in the substrate to form ettringite in the adhesive layer. This causes weakness of the adhesive/substrate interface and leads to failure in bonding the tiles to the substrate. In order to solve this problem it has hitherto been proposed to apply a primer layer to the substrate before application of the adhesive in order to form a chemical barrier to prevent ettringite formation. The application of such a barrier layer is, however, laborious and increases expense, as well as sometimes decreasing the strength of the bond between the tile and the substrate.

EP-A-0 320 982 describes tile adhesives and grouts containing calcium sulphate and an aluminate-free cement.

Tile adhesives are generally used in two types of application. Thin-bed applications are usually used for applying tiles to substantially uniform surfaces, such as walls, and in this application the thickness of the adhesive layer is up to 3 mm. Thick-bed applications, where the thickness of the adhesive layer is greater than 3 mm, are used where the surface of the substrate is uneven, such as on floors or poorly finished walls.

We have now found it possible to formulate a calcium sulphate-based adhesive, e.g. for bonding a ceramic tile in thin- or thick-bed applications, that does not suffer from the above mentioned disadvantages when used with a gypsum-based substrate.

References to "ceramic tiles" herein are intended to encompass not only ceramic tiles *per se* but also other hard surface coverings such as natural or re-constituted stones and mosaics.

According to one aspect, the invention provides a composition for admixing with water to form an adhesive, comprising:

- (A) anhydrous and/or partially hydrated calcium sulphate;
- (B) a hardening-rate modifier to regulate the rate of setting of the composition when admixed with water;
- (C) a water-retention aid;
- (D) a rheology modifier; and
- (E) a water-soluble or redispersible polymer resin.

Various preferred features and embodiments of the invention are described below by way of non-limiting illustration.

The compositions of the invention are generally in the form of dry powders that are admixed with water immediately prior to use to form an adhesive paste that can be used in thick- or thin-bed applications. The amount of water added to the composition of the invention is therefore generally chosen to enable the adhesive to be readily applied uniformly to the substrate with little or no slippage of the ceramic tile before hardening of the adhesive occurs. The compositions of the invention form adhesives that avoid ettringite formation when applied to a gypsum-base substrate and therefore have high bond strengths.

Component (A) of the compositions of the invention is anhydrous or partially hydrated calcium sulphate, e.g. calcium sulphate hemihydrate in α - or β - form. For reasons of cost and ready availability, it is preferred to use calcium sulphate hemihydrate (β - form) as a fine powder.

The compositions of the invention contain (B) a hardening-rate modifier to regulate the rate of setting of the composition when admixed with water. Without such a hardening-rate modifier, compositions containing anhydrous calcium sulphate set too slowly when admixed with water, and compositions containing partially hydrated calcium sulphate set too quickly. Materials that can be used for this purpose include: alkali metal salts to accelerate the rate of setting when the compositions contain anhydrous calcium sulphate; and/or organic acids and/or salts thereof to retard the rate of setting when the compositions contain a partially

hydrated calcium sulphate. Examples of organic acids that may be used include citric acid and other carboxylic acids such as tartaric acid, and their salts. In some circumstances, the resin component (E) of the compositions may comprise a material that acts as a hardening retarder, e.g. where component (E) contains an organic acid or salt, and in these cases component (E) may have a dual function and it may not be necessary to add additional component (B).

Other materials that serve to regulate the rate of setting of calcium sulphate-containing compositions are known to those skilled in the art.

The compositions of the invention include (C) a water retention aid. Materials that can be used for this purpose include cellulose ethers, starch ethers, natural or synthetic gums and the like. Examples of cellulose ethers include: hydroxypropyl methyl cellulose, commercially available as Methocels (Dow Chemical Company) or Walocels (Wolff Walstrode AG); carboxymethyl cellulose ethers, commercially available from Courtaulds Chemicals and Wolff Walstrode AG; and methyl hydroxyethyl cellulose ethers, commercially available as Tylose (Hoechst) or Culminal (Aqualon).

The compositions also include (D) a rheology modifier to allow the compositions to be readily applied to a substrate when admixed with water in use and which help to prevent slippage of the tiles while the adhesive is setting. Materials that can be used for this purpose include the above-mentioned cellulose ethers, starch ethers and natural or synthetic gums, as well as inorganic materials such as bentonite clays, wollastonites, attapulgites and the like. Bentonite clays are commercially available in the Bentone range from Redland Minerals, and attapulgites are commercially available in the Attagel range from Lawrence Industries. It will be appreciated that when the compositions of the invention contain cellulose ethers, starch ethers and/or natural or synthetic gums, these may serve as both water-retention aids (C) and rheology modifiers (D).

The compositions of the invention include (E) a water-soluble or redispersible polymer resin. The resin generally serves to improve the cohesive and adhesive strength of the compositions when admixed with water in use. Examples of resins

that may be utilised in the compositions of the invention include water-soluble resins, such as polyvinyl alcohol, and preferably redispersable polymer powder resins, e.g. derived from dispersions of : vinyl resins; styrene resins; copolymers of vinyl laurate, vinyl chloride and/or vinyl acetate and ethylene; vinyl acetate; copolymers of vinyl acetate and vinyl ^(Versatic is a registered trade mark) versatate; styrene/acrylic copolymers; or resins derived from dispersions of styrene and butyl acetate or styrene and butadiene. The resins may optionally be silanated, e.g. silane groups may be added during polymerisation, since this has been found to increase the water resistance of the composition.

Suitable resins include: Goshenol water-soluble polyvinyl alcohol polymers; and redispersible polymer powders such as Rhophlex resins from Rohm and Haas, particularly Rhophlex DP 2605; Elotex resins from Elotex AG, particularly Elotex 1080, Elotex 50V/906, Elotex WS45 or WS73, Elotex AP200, Elotex BN0107 and Elotex WS101E; Vinnapas resins from Wacker Chemicals, particularly Vinnapas RI 532Z, Vinnapas RE5452, 546Z and 547Z, Vinnapas RI 538Z; Mowilith powder resins from Hoechst Limited, particularly Mowilith LDM 2072P, LDM 2070O, DM117P and LDM 2040P; Acronal DS6200 from BASF (UK) Limited; PAV 27, PAV 29 and Rhodopas PSB 54 from Rhone-Poulenc; and DLP 110 and DLP 120 from Dow Europe.

The compositions of the invention may optionally further include calcium hydroxide, usually in powder form, in order to improve workability of the compositions when admixed with water for use. The incorporation of calcium hydroxide also serves as a pH increaser and rapidly activates resin component (E).

It is also sometimes convenient to optionally add fibres, fillers, antifoaming agents and/or wetting agents to the compositions of the invention. The presence of fibres serves to improve the coherence and resistance to slippage of the adhesive before it hardens and sets. Examples of fibres that may be used include natural or synthetic organic materials such as cotton, wool, nylon, polyethylene or polypropylene fibres, as well as inorganic fibres such as glass fibres.

Fillers that may be incorporated into the compositions of the invention include fine particle size inorganic materials such as silica sand, calcium carbonate (e.g. in the

Fillers that may be incorporated into the compositions of the invention include fine particle size inorganic materials such as silica sand, calcium carbonate (e.g. in the form of ground limestone or calcite) or calcium magnesium carbonates (dolomites). The use of fillers is particularly preferred where the compositions are to be used in thick-bed applications since they help to reduce cost and enhance the workability of the adhesive.

Component (A) is conveniently present in an amount of 10-80% by weight of the dry composition of the invention. Component (B) is conveniently present in an amount of 0.01 to 2% by weight. Component (C) is conveniently present in an amount of from 0.05 to 3% by weight. Component (D) is conveniently present in an amount up to 5% by weight. Component (E) is conveniently present in an amount of 0.5 to 10% by weight.

When present, calcium hydroxide is conveniently present in an amount up to 10% by weight of the composition. Optional fillers may conveniently be present in an amount of from 10 to 50% by weight. Fibres may optionally be present in an amount of from 0.1 to 2% by weight.

Shortly before use, the compositions of the invention are mixed with sufficient water to form a smooth, firm adhesive paste which may be applied to a substrate before tiles are applied thereto. The adhesive of the invention allows sufficient working time before hardening and setting, and during this period little or no slippage of the tiles occurs. The ability to provide little slippage is especially advantageous when tiles are to be applied to walls. The adhesive provides a high bond strength, and may be applied to a gypsum-based substrate without first applying a primer layer. In some cases, however, it may be desirable first to apply a primer layer, e.g. to stabilise a cracked or crumbling substrate, but this is not necessary to prevent ettringite formation.

The following non-limiting examples serve to illustrate the invention.

FORMULATION	1 comparison	2 comparison	3	4	5
alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	80	80	50		
beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$				40	35
Fine silica sand			20	20	20
Ground limestone	18	18	20	20	25
Calcium hydroxide			2.4	10	5
Redispersible resin-1	2				
ditto - 2		2			
ditto - a blend			5	5	3
Cellulose ethers			2.5	3	1.5
Clay				1.5	9.0
Organic acid			0.1	0.5	1.0
Cellulose fibres					0.5
Water	22	23	27	27	26

RESULTS		All tested and stored at 23°C/50% RH.			
Setting time	over 5 days	11 mins	19 mins	41 mins	60 mins
Open time		2 mins	11 mins	19 mins	22 mins
Workability		Poor	Good	Good	V.good
Slip			1 mm	1 mm	0.5 mm
Bond Stengths:					
(a) Tensile to CEN pr EN 1348 in N/mm^2			0.7	0.72	0.7
(b) Shear to BS 5980					
@ 14 days		9.5	>20	>20	18.0
@ 24 hours in kN					10.00

For further comparison, an adhesive was prepared containing:

α -CaSO₄.½ H₂O - 100 gms

(Calcium sulphate alpha hemihydrate)

Water - 24 gms.

This set hard in 5 mins. and was difficult to make up for shear test samples. It was tested after 14 days in air to the shear-test requirements of British standard 5980, and gave only 2 kN (Minimum pass level 8.9 kN).

CLAIMS

1. A composition for admixture with water to form an adhesive, comprising:
 - (A) anhydrous and/or partially hydrated calcium sulphate;
 - (B) a hardening-rate modifier to regulate the rate of setting of the composition when admixed with water;
 - (C) a water-retention aid;
 - (D) a rheology modifier; and
 - (E) a water-soluble or redispersible polymer resin.
2. A composition according to claim 1 wherein component (A) comprises calcium sulphate hemihydrate (beta form).
3. A composition according to either of claims 1 or 2 wherein component (B) comprises one or more alkali metal salts, organic acids and/or salts thereof.
4. A composition according to any preceding claim wherein component (C) comprises one or more cellulose ethers, starch ethers and/or natural or synthetic gums.
5. A composition according to any preceding claim wherein component (D) comprises one or more cellulose ethers, starch ethers, natural or synthetic gums, bentonite clays, wollastonites and/or attapulgites.
6. A composition according to any preceding claim wherein component (E) comprises one or more: polyvinyl alcohols; vinyl resins; styrene resins; copolymers of vinyl laurate, vinyl chloride and/or vinyl acetate and ethylene; vinyl acetate; copolymers of vinyl acetate and vinyl versatate; styrene/acrylic copolymers; or resins derived from dispersions of styrene and butyl acetate or styrene and butadiene; which may optionally be silanated.
7. A composition according to any preceding claim which additionally contains calcium hydroxide.

8. A composition according to any preceding claim which additionally contains fibres and/or fillers.
9. An adhesive composition comprising water in admixture with a composition as defined in any preceding claim.

AMENDMENTS TO THE CLAIMS HAVE BEEN FILED AS FOLLOWS

1. A method of adhering a ceramic tile to a gypsum-based substrate wherein the adhesive is formed by admixing with water a composition comprising:
 - (A) anhydrous and/or partially hydrated calcium sulphate;
 - (B) a hardening-rate modifier to regulate the rate of setting of the composition when admixed with water;
 - (C) a water-retention aid;
 - (D) a rheology modifier; and
 - (E) a water-soluble or redispersible polymer resin.
2. A method according to claim 1 wherein component (A) comprises calcium sulphate hemihydrate (beta form).
3. A method according to either of claims 1 or 2 wherein component (B) comprises one or more alkali metal salts, organic acids and/or salts thereof.
4. A method according to any preceding claim wherein component (C) comprises one or more cellulose ethers, starch ethers and/or natural or synthetic gums.
5. A method according to any preceding claim wherein component (D) comprises one or more cellulose ethers, starch ethers, natural or synthetic gums, bentonite clays, wollastonites and/or attapulgites.
6. A method according to any preceding claim wherein component (E) comprises one or more: polyvinyl alcohols; vinyl resins; styrene resins; copolymers of vinyl laurate, vinyl chloride and/or vinyl acetate and ethylene; vinyl acetate; copolymers of vinyl acetate and vinyl versatate; styrene/acrylic copolymers; or resins derived from dispersions of styrene and butyl acetate or styrene and butadiene; which may optionally be silanated.
7. A method according to any preceding claim which additionally contains calcium hydroxide.

8. A method according to any preceding claim which additionally contains fibres and/or fillers.

9. Use of a composition comprising:

(A) anhydrous and/or partially hydrated calcium sulphate;

(B) a hardening-rate modifier to regulate the rate of setting of the composition when admixed with water;

(C) a water-retention aid;

(D) a rheology modifier; and

(E) a water-soluble or redispersible polymer resin in admixture with water to form an adhesive for adhering a ceramic tile to a gypsum-based substrate.



Application No: GB 9720960.5
Claims searched: 1 to 9

Examiner: Miss M. M. Kelman
Date of search: 27 January 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C1H HCC HXE HXG HXX

Int Cl (Ed.6): C04B 28/14

Other: ONLINE: CLAIMS, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X,Y	GB 2140794 A UNITED STATES GYPSUM see the Examples	X:1-6,8,9 Y:7
X,Y	EP 0496682 A1 PLATRES LAFARGE see the claims and Examples 3 to 20	X:1,2,4,5, 6,8,9 Y:7
Y	EP 0320982 A1 PCI POLYCHEMIE see the claims and Example 6	7
X,Y	EP 0303071 A1 RIGIPS see the whole document	X:1,2,4,5, 6,8,9 Y:7
X,Y	EP 0094507 A2 GEBR. KNAUF WESTDEUTSCHE GIPSWERKE see the whole document	X:1,3,4,5, 6,8,9 Y:7
X,Y	US 5277712 A LOUISIANA-PACIFIC see the claims and Examples	X:1,3,4,5, 6,8,9 Y:7
X,Y	JPO & JAPIO Abstract No. 03008240 & JP 010305840 (MARUSEN) 11 December 1989 see abstract	X:1,3,4,5, 6,8,9 Y:7
X,Y	JPO & JAPIO Abstract No. 03008239 & JP010305839 (MARUSEN) 11 December 1989 see abstract	X:1-6,8,9 Y:7

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.